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DECISION OF REJECTION IN THE FIRST EXAMINATION

Mailed: September 2, 2003

Application No.: 090115279

International Classification 7th ed.: H01L 21/304

Title of the Invention: Substrate Washing Method and Substrate Washing Apparatus

Applicant: KABUSHIKI KAISHA TOSHIBA

Filing Date: June 22, 2001

Priority: June 22, 2000 JP 2000-190696

Decision:

TEXT: The present invention is unpatentable.

BASIS: Section 20 (2) of the Patent Law.

REASONS:

1. The present invention titled "Substrate Washing Method and Substrate Washing Apparatus" provides a method for washing a substrate. A substrate is washed in an acidic solution, and then in a basic solution in the same washing apparatus. The present invention is characterized in that the acidic solution remaining on the surface of the substrate is efficiently removed by the neutralization reaction of the acid and the base.

2. Taiwanese Patent Publication No. 391034 disclosed on May 21, 2000 titled "Substrate Washing Method" (attached) discloses that a substrate is washed in a basic solution, and then in an acidic solution in the same washing apparatus, so that the basic solution remaining on the surface of the substrate is efficiently removed by the neutralization reaction of the acid and the base. The method of the present invention is to efficiently remove the chemical solution remaining on the surface of the substrate by the neutralization reaction of the acid and the base. This is different from the reference only in the order of using the basic and acidic solutions. Thus, the present invention lacks an inventive step, since it can be easily accomplished by a person skilled in the art.

For the reasons stated above, since the present invention fails to satisfy the legal requirements for patent, it is rejected under Section 20 (2) of the Patent Law.

Note: If the applicant is dissatisfied with the above decision, it can request reexamination by filing a reason for request of reexamination in duplicate together with an official fee of NT\$6,000 with the Patent Office within 30 days of the next day of the mailing date of this decision (if the number of pages of the specification and drawings exceeds 50, an official fee of NT\$500 shall be paid for every additional 50 pages: if the number of pages is less than 50, it shall be counted as 50).

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經濟部智慧財產局專利核駁審定書

受文者：東芝股份有限公司（代理人：陳長文先生）

地址：臺北市松山區敦化北路二〇一號七樓

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- 一、申請案號數：〇九〇一一五二七九
- 二、發明名稱：基板洗淨方法及基板洗淨裝置
- 三、申請人：

名稱：東芝股份有限公司

地址：日本

四、專利代理人：

姓名：陳長文先生

地址：臺北市松山區敦化北路二〇一號七樓

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七、審查人員姓名：謝志偉 委員

八、審定內容：

主文：本案應不予專利。

依據：專利法第二十條第二項。

理由：

(一) 本案「基板洗淨方法及基板洗淨裝置」係提供一種基板洗淨方式，其特徵為：先利用酸性藥液洗淨被洗淨的基板，在於同一洗淨裝置內利用鹼性藥液清洗基板，藉由酸鹼中和的反應以有效除去被洗淨基板上殘留的酸性藥液。

(二) 經查民國八十九年五月二十一日公告之中華民國專利公告號第三九一〇三四號案「清潔基板的方法」(引證附件)所示，該引證案已揭示利用鹼性藥液洗淨被洗淨的基板，再利用酸性藥液清洗基板，藉由酸鹼中和的反應以有效除去被洗淨基板上殘留的鹼性藥液；相較引證案，本案所述之方式係為藉由酸鹼中和的反應以有效除去被洗淨基板上殘留的藥液，其差異處僅在酸鹼溶液的順序不同，為熟悉該項技術者所能輕易知悉並完成，故不具進步性。

據上論結，本案不符法定專利要件，爰依專利法第二十條第二項，審定如主文。

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局長 蔡練生



依照分層負責規定授權單位主管執行

如不服本審定，得於文到之次日起三十日內，備具再審查理由書一式二份及規費新台幣陸仟元整（專利說明書及圖式合計在五十頁以上者，每五十頁加收新台幣五百元，其不足五十頁者以五十頁計），向本局申請再審查。

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發明

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[54]名稱：清潔基板的方法

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[72]發明人：

嵯峨幸一郎

日本

小谷田作夫

日本

服部毅

日本

[71]申請人：

蘇妮股份有限公司

日本

[74]代理人：林志剛 先生

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[57]申請專利範圍：

1.一種清潔基板表面之方法，其中清潔該基板方法之第一步驟包括將該基板表面上所形成之天然氧化物膜加以去除之步驟，在去除該天然氧化物膜之後，包括至少

用鹼性溶液清洗之第二步驟，

用酸性溶液清洗之第三步驟，以及

以濕式蝕刻而去除因該第三清洗步驟所形成之 SiO₂ 膜之第四步驟，且

其中該鹼性溶液包括氫、過氧化氫，以及純水。

2.如申請專利範圍第1項之清潔基板之方法，其中該去除天然氧化物膜之步驟包括將該基板浸入一含有氫氟酸之溶液中。

3.如申請專利範圍第2項之清潔基板之方法，其中該氫氟酸溶液具有0.5重量百分比之濃度，且其中浸入時間約1分鐘。

4.如申請專利範圍第2項之清潔基板之方

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法，其中該含氫氟酸之溶液包括一含有氫氟酸及氟化銨之緩衝氫氟酸溶液。

5.如申請專利範圍第4項之清潔基板之方法，其中該緩衝氫氟酸包含0.1重量百分比氫氟酸及60重量百分比氟化銨。

6.如申請專利範圍第1項之清潔基板之方法，其中該去除天然氧化物膜之步驟包括將基板暴露於一含氫氟酸之蒸氣中。

7.如申請專利範圍第6項之清潔基板之方法，其中該含氫氟酸之蒸氣包括一含有氫氟酸及氟化銨之緩衝氫氟酸的蒸氣。

8.如申請專利範圍第7項之清潔基板之方法，其中該緩衝氫氟酸之蒸氣係藉由加熱一含有0.1重量百分比氫氟酸及60重量百分比氟化銨之水溶液而形成。

9.如申請專利範圍第8項之清潔基板之方法，其中該緩衝氫氟酸之蒸氣壓力係為常壓。

10.如申請專利範圍第9項之清潔基板之方法，其中該矽基板係暴露於該含緩衝

METHOD OF CLEANING SUBSTRATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a method of
cleaning a substrate, more particularly relates to a
method of cleaning a substrate which enables the organics
or inorganics or other contaminants adhering to the
surface of the substrate to be effectively removed from
10 the substrate surface.

2. Description of the Related Art

 In the process of production of a semiconductor
device, contamination can occur having a detrimental
effect on the operating characteristics of the
15 semiconductor device. One type of contamination is the
minute amount of organics adsorbed on the surface of the
silicon substrate. This minute amount of organics ends up
adsorbed to the surface of the semiconductor device even
when just allowing the silicon substrate to stand in a
20 dust-free atmosphere or plastic box.

 In the cleaning methods of the related art, it
is not possible to effectively remove the minute amount of
organics adsorbed to the surface of the silicon substrate.
Therefore, the minute amount of organics which could not
25 be removed remained on the surface of the silicon

substrate and suffers from the disadvantage on production.

SUMMARY OF THE INVENTION

5 ✓ An object of the present invention is to provide a method of cleaning a substrate enabling removal of even the minute amount of adsorbed organics present on the substrate surface.

10 To achieve the above object, the present invention provides a method of cleaning the surface of a substrate wherein the first step of the process of cleaning the substrate, including a step of cleaning the surface of the substrate by an acidic solution, oxidizing solution, or alkaline solution, is a step of removing the natural oxide
15 film formed on the surface of the substrate.

20 Preferably, the natural oxide film is removed by immersing the substrate in a solution containing hydrofluoric acid. The solution containing hydrofluoric acid may be a hydrofluoric acid solution of a
25 concentration of 0.5 percent by weight and the time of immersion may be approximately 1 minute. Alternatively, the solution containing hydrofluoric acid may be a buffered hydrofluoric acid solution containing hydrofluoric acid and ammonium fluoride. In this case, the buffered hydrofluoric acid solution preferably is

comprised of 0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride.

Preferably, the alkaline solution is comprised of ammonia, hydrogen peroxide, and pure water.

5 Alternatively, the natural oxide film may be removed by exposing the substrate in a vapor containing hydrofluoric acid. In this case, preferably the vapor containing hydrofluoric acid is a vapor of a buffered hydrofluoric acid containing hydrofluoric acid and
10 ammonium fluoride. Preferably, the vapor of the buffered fluoride acid is formed by heating an aqueous solution of 0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride. In this case, the pressure of the vapor of the buffered hydrofluoric acid is
15 preferably made ordinary pressure and the silicon substrate is preferably exposed in the vapor containing the buffered hydrofluoric acid for 0.5 to approximately 1 minute.

20 Preferably, after the step of removing the natural oxide film, there are further provided a step of cleaning by an alkaline solution and a step of cleaning by an acidic solution.

BRIEF DESCRIPTION OF THE DRAWINGS

25 These and other objects and features of the present

invention will become apparent from the following description of the preferred embodiments made with reference to the attached drawings, in which

Fig. 1 is a flow chart of the method of cleaning a silicon substrate according to the related art,

Fig. 2 is a flow chart of the method of cleaning a silicon substrate according to an embodiment of the present invention,

Figs. 3A to 3D are schematic cross-sectional views of the state of the surface of a substrate at the steps of the method of cleaning a silicon substrate according to an embodiment of the present invention, and

Fig. 4 is a graph comparing the cleaning effect of a substrate by the method of cleaning a silicon substrate according to embodiments of the present invention and the cleaning effect of the methods of cleaning according to the related art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before describing the present invention, a brief explanation will be made of one of the related arts by way of reference.

The surface of silicon substrates has been cleaned in the related art by the process shown in the flow chart of Fig. 1.

As shown in Fig. 1, first, at step 1, the surface is cleaned using a strong acid or a strong oxidizing agent (sulfuric acid + hydrogen peroxide, fuming nitric acid, ultra-pure water with ozone, etc.) for the purpose of removing the organics from the surface of the silicon substrate. Next, at step 2, pure water is used to rinse the surface to wash off the cleaning solution of the previous step, then at step 3 the surface is cleaned using an alkaline cleaning solution (ammonia + hydrogen peroxide + pure water).

Next, at step 4, the surface is rinsed and cleaned with pure water to wash off the cleaning solution of the previous step, then at step 5 the surface is cleaned using an acidic cleaning solution (hydrochloric acid + hydrogen peroxide + pure water etc.) for the purpose of removing the heavy metals. Next, at step 6, the surface is rinsed and cleaned by pure water to wash off the cleaning solution of the previous step, then at step 7, the surface is wet etched using hydrofluoric acid or buffered hydrofluoric acid for the purpose of removing the natural oxide film formed on the silicon substrate surface by the cleaning solution. Next, at step 8, the surface of the silicon surface is stripped of water and dried.

In the cleaning method of the above related art, however, the present inventors found by experiments that

it was not possible to effectively remove the minute amount of organics adsorbed to the surface of the silicon substrate. That is, while it was possible to reduce the large amount of adsorbed organics to a minute amount by the cleaning by the strong acid or strong oxidizing agent applied first in the above cleaning method of the related art, it was not possible to reduce the minute amount of the adsorbed organics to substantially close to zero.

Note that in the process of the related art, the treatment by the hydrofluoric acid or buffered hydrofluoric acid was performed as a later step of the cleaning by the acidic solution, but this treatment was for removing the oxide film formed on the surface of the silicon by the cleaning by the oxidizing solution.

Therefore, the minute amount of organics which could not be removed by the strong acid or strong oxidizing agent remains on the surface of the silicon substrate even after the stripping and drying treatment of step 8 and becomes a problem in production.

The present invention provides a method of cleaning the surface of a substrate wherein the first step of the process of cleaning the substrate including a step of cleaning the surface of the substrate by an acidic solution, oxidizing solution, or alkaline solution, comprises a step of removing the natural oxide film formed

on the surface of the substrate.

The natural oxide film is removed by immersing the substrate in a solution containing hydrofluoric acid or exposing the substrate in vapor containing hydrofluoric acid. As the solution containing the hydrofluoric acid, use may be made of an aqueous solution of hydrofluoric acid, a buffered hydrofluoric acid solution containing hydrofluoric acid and ammonium fluoride, etc. As the vapor containing the hydrofluoric acid, use may be made of a vapor of an aqueous solution of hydrofluoric acid, a vapor of a buffered hydrofluoric acid containing hydrofluoric acid and ammonium fluoride, etc.,

When using a hydrofluoric acid, the concentration of the hydrofluoric acid is preferably at least 0.1 percent by weight and the treatment time is for example 30 seconds to 3 minutes. When using a buffered hydrofluoric acid, the concentration of the hydrofluoric acid is 0.05 to 10 percent by weight. The ratio of weight of the ammonium fluoride (NH_4F) to the hydrofluoric acid (HF) is about 1:200 to 600. The treatment time is for example 30 seconds to 3 minutes.

After the step of removing the natural oxide film, at least a step of cleaning by an alkaline solution and a step of cleaning by an acidic solution are performed.

The substrate to be cleaned by the method of cleaning

of the present invention is not particularly limited, but for example may be a silicon substrate, gallium arsenide substrate, or other semiconductor substrate or other substrate.

5 In the method of cleaning a substrate according to the present invention, the first step of cleaning is to remove the natural oxide film formed on the surface of the substrate by hydrofluoric acid, buffered hydrofluoric acid, etc., so it is possible to effectively remove the
10 minute amount of organics and inorganics adsorbed on the natural oxide film.

Next, it is possible to remove the particulates on the substrate surface by cleaning by an alkaline solution (ammonia + hydrogen peroxide + pure water). Further, it is
15 possible to remove the heavy metals on the surface of the substrate by cleaning by an acidic solution (hydrochloric acid + hydrogen peroxide + pure water etc.)

When cleaning the substrate by the acidic solution, an oxide film is sometimes formed on the surface of the
20 substrate, but this film can be removed by a final step of wet etching by hydrofluoric acid, buffered hydrofluoric acid, etc.

As a result, it is possible to substantially completely remove the organics adsorbed on the surface of
25 the substrate before cleaning and possible to easily

obtain a substrate with excellent surface conditions. That is, the method of cleaning of the present invention enables one to obtain an extremely clean semiconductor wafer or other substrate, eliminates the contamination by the minute amount of organics in the later film-forming, etching, exposure, and other processes, and thereby enables production of extremely high quality semiconductor devices with a good yield.

In particular, silicon wafers and other substrates are sometimes placed in plastic boxes for storage or transportation etc. The plasticizers, cross-linking agents, antioxidants, etc. contained in the plastic sometimes are absorbed on the oxide film on the surface of the substrates. In the method of cleaning of the related art, it had not been possible to effectively remove these minute amounts of organics from the substrate surface.

According to the method of cleaning of the present invention, it is possible to substantially completely remove the organics adsorbed on the surface of the substrates before cleaning. The minute amounts of organics able to be removed by the method of the present invention are not particularly limited, but include for example substances easily adhering to natural oxide films such as diacetylbenzene and other cross-linking agents, dibutyl phthalate (DBP), dioctyl phthalate, and other

plasticizers, di-tertiary-butyl-p-cresol (BHT), and other antioxidants.

The method of cleaning a substrate according to the present invention will be explained in further detail
5 below based on the embodiments shown in the figures.

Figure 2 is a flow chart of the method of cleaning a silicon substrate according to an embodiment of the present invention, Figs. 3A to 3D are schematic cross-sectional views of the state of the surface of a substrate
10 at the steps of the method of cleaning a silicon substrate according to an embodiment of the present invention, and Fig. 4 is a graph comparing the cleaning effect of a substrate by the method of cleaning a silicon substrate according to embodiments of the present invention and the
15 cleaning effect of the methods of cleaning according to the related art.

FIRST EMBODIMENT

Next, a detailed explanation will be made of a first embodiment of the present invention.

20 Various contaminants are present on the surface of a silicon substrate before it is subjected to a film-forming, photolithographic, or other process. The state of adsorption of the contaminants is for example as shown in Fig. 3A. That is, a natural oxide film 13 containing metal
25 impurities 14 is present on the surface of the silicon

substrate 11. Further, organics 12 are adsorbed to that surface.

If the organics 12 are not removed in the first step of the cleaning of the surface of the silicon substrate, the surface will remain covered by the organics 12 and therefore it will be difficult to remove the heavy metals and other metal impurities 14 in the later steps.

Therefore, in this embodiment, as shown in Fig. 2, in the first step of the cleaning, that is, step 20, the silicon substrate is immersed in an aqueous solution of hydrofluoric acid. The aqueous solution of hydrofluoric acid has a concentration of hydrofluoric acid (HF) of 0.5 percent by weight (0.25M/liter) in this embodiment. The substrate is immersed for approximately 1 minute.

As a result of the treatment by hydrofluoric acid, as shown in Fig. 3B, the adsorbed organics 12 can be removed together with the natural oxide film 13. The metal impurities 14 remain on the surface of the silicon substrate.

An experiment was performed as follows to show that the impurities adsorbed on the surface of the silicon substrate could be substantially completely removed by the treatment by hydrofluoric acid.

The hydrofluoric acid-treated silicon substrate was heated to 400°C, the desorbed gas was condensed, and the

content of the adsorbed organics was analyzed by gas chromatography and mass spectrophotometry (GC/MS). The results are shown in Fig. 4. In Fig. 4, the vertical axis shows the content of the diacetylbenzene and dibutyl phthalate (DBP). The horizontal axis shows the methods of cleaning of the related art and present invention. As shown in Fig. 4, it was confirmed that the present invention enabled the approximately 210 ng content of the diacetylbenzene and the approximately 20 ng content of the dibutyl phthalate to be substantially completely removed.

As opposed to this, the related arts of O₂ Asher, cleaning by an aqueous solution of ammonia + hydrogen peroxide (APM), cleaning by an aqueous solution of sulfuric acid + hydrogen peroxide (SPM), and cleaning by fuming nitric acid (HNO₃) were not able to completely remove the organics.

In the present embodiment, after the treatment by the hydrofluoric acid, the substrate is rinsed by pure water to wash off the cleaning solution of the previous step at step 21 of Fig. 2, then is cleaned using an alkaline (ammonia + hydrogen peroxide + pure water, etc.) cleaning solution for the purpose of removing particulates at step 22.

Next, at step 23, the substrate is rinsed and cleaned by pure water to wash off the cleaning solution of the

previous step, then at step 24 it is cleaned using an acidic (hydrochloric acid + hydrogen peroxide + pure water etc.) cleaning solution. The cleaning by this acidic solution removes the metal impurities 14 from the surface of the silicon substrate 11 shown in Fig. 3B. However, the cleaning by the acidic solution, as shown in Fig. 3C, results in the formation of a clean natural silicon oxide film 15 on the surface of the silicon substrate 11.

Next, at step 25 shown in Fig. 2, the surface is rinsed and cleaned by pure water to wash off the cleaning solution of the previous step, then at step 26 hydrofluoric acid or buffered hydrofluoric acid is used to wet etch the substrate surface. This wet etching, as shown in Fig. 3D, enables the removal of the natural oxide film 15 formed on the surface of the silicon substrate by the cleaning solution. Next, at step 27 shown in Fig. 2, the surface of the silicon substrate is stripped of water and dried.

In the method of cleaning of a substrate according to this embodiment, since the first step of cleaning is to remove the natural oxide film formed on the surface of the substrate by hydrofluoric acid, it is possible to efficiently remove the minute amount of adsorbed organics adhering to the natural oxide film.

SECOND EMBODIMENT

Next, an explanation will be made of a second embodiment of the present invention.

The same procedure is followed as in the first embodiment to clean the silicon substrate except that use is made of buffered hydrofluoric acid instead of hydrofluoric acid at step 20 shown in Fig. 2. The buffered hydrofluoric acid used is an aqueous solution of 0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride. The substrate is immersed for approximately 1 minute.

In the same way as the case of the first embodiment, the content of the organics remaining on the surface of the silicon substrate after treatment by the buffered hydrofluoric acid was examined. As shown in Fig. 4, it was almost 0.

In the method of cleaning of a substrate according to this embodiment, since the first step of cleaning is to remove the natural oxide film formed on the surface of the substrate by buffered hydrofluoric acid, it is possible to efficiently remove the minute amount of adsorbed organics adhering to the natural oxide film.

THIRD EMBODIMENT

Next, an explanation will be made of a third embodiment of the present invention.

The same procedure is followed as in the first embodiment to clean the silicon substrate except that use is made of a vapor of hydrofluoric acid instead of a solution of hydrofluoric acid at step 20 shown in Fig. 2.

5 The vapor of hydrofluoric acid used is obtained by heating an aqueous solution of 0.5 percent by weight of hydrofluoric acid (0.25M/liter). The temperature of the vapor is ordinary temperature and the pressure is ordinary pressure. The substrate is exposed to the vapor for 0.5 to
10 approximately 1 minute.

In the same way as the case of the first embodiment, the content of the organics remaining on the surface of the silicon substrate after treatment by the vapor of hydrofluoric acid was examined. As shown in Fig. 4, it was
15 almost 0.

In the method of cleaning of a substrate according to this embodiment, since the first step of cleaning is to remove the natural oxide film formed on the surface of the substrate by vapor of hydrofluoric acid, it is possible to
20 efficiently remove the minute amount of adsorbed organics adhering to the natural oxide film.

FOURTH EMBODIMENT

Next, an explanation will be made of a fourth embodiment of the present invention.

25 The same procedure is followed as in the first

embodiment to clean the silicon substrate except that use is made of a vapor of buffered hydrofluoric acid instead of the solution of hydrofluoric acid at step 20 shown in Fig. 2. The vapor of buffered hydrofluoric acid used is
5 obtained by heating an aqueous solution of 0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride. The temperature of the vapor is ordinary temperature and the pressure is ordinary pressure. The substrate is exposed to the vapor for 0.5 to
10 approximately 1 minute.

In the same way as the case of the first embodiment, the content of the organics remaining on the surface of the silicon substrate after treatment by the vapor of buffered hydrofluoric acid was examined. As shown in Fig.
15 4, it was almost 0.

In the method of cleaning of a substrate according to this embodiment, since the first step of cleaning is to remove the natural oxide film formed on the surface of the substrate by vapor of buffered hydrofluoric acid, it is
20 possible to efficiently remove the minute amount of adsorbed organics adhering to the natural oxide film.

For example, the treatment performed at step 20 shown in Fig. 2 is not limited to treatment by immersing the substrate in a solution containing hydrofluoric acid or
25 treatment by exposing the substrate in vapor containing

hydrofluoric acid. Another treatment may be used so long as it enables the natural oxide film formed on the surface of the silicon substrate to be removed together with the organics on the surface.

5 As explained above, according to the present invention, it is possible to substantially completely remove the organics adsorbed on the surface of the substrate before cleaning and therefore possible to easily obtain a substrate with an excellent surface state. That
10 is, the method of cleaning of the present invention enables one to obtain an extremely clean semiconductor wafer or other substrate, eliminates the contamination by the minute amount of organics in the subsequent film-forming, etching, exposure, or other processes, and
15 thereby enables production of extremely high quality semiconductor devices with a good yield.

What is claim is:

1. A method of cleaning a surface of a substrate, wherein a first step of the process of cleaning the substrate including a step of cleaning the surface of the substrate by an acidic solution, oxidizing solution, or alkaline solution, comprises a step of removing the natural oxide film formed on the surface of the substrate.

2. A method of cleaning a substrate as set forth in claim 1, wherein the natural oxide film is removed by immersing the substrate in a solution containing hydrofluoric acid.

3. A method of cleaning a substrate as set forth in claim 2, wherein the hydrofluoric acid solution has a concentration of 0.5 percent by weight and wherein the time of immersion is approximately 1 minute.

4. A method of cleaning a substrate as set forth in claim 1, wherein the alkaline solution comprises ammonia, hydrogen peroxide, or pure water.

5. A method of cleaning a substrate as set forth in claim 2, wherein solution containing hydrofluoric acid comprises a buffered hydrofluoric acid solution containing hydrofluoric acid and ammonium fluoride.

6. A method of cleaning a substrate as set forth in claim 5, wherein the buffered hydrofluoric acid comprises

0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride.

7. A method of cleaning a substrate as set forth in claim 1, wherein the natural oxide film is removed by exposing the substrate in a vapor containing hydrofluoric acid.

8. A method of cleaning a substrate as set forth in claim 7, wherein the vapor containing hydrofluoric acid comprises a vapor of buffered hydrofluoric acid containing hydrofluoric acid and ammonium fluoride.

9. A method of cleaning a substrate as set forth in claim 7, wherein the vapor of buffered fluoride acid is formed by heating an aqueous solution of 0.1 percent by weight of hydrofluoric acid and 60 percent by weight of ammonium fluoride.

10. A method of cleaning a substrate as set forth in claim 9, wherein the pressure of the vapor of buffered hydrofluoric acid is made ordinary pressure.

11. A method of cleaning a substrate as set forth in claim 10, wherein the silicon substrate is exposed in the vapor containing the buffered hydrofluoric acid for 0.5 to approximately 1 minute.

12. A method of cleaning a substrate as set forth in claim 1, including, after the step of removing the natural oxide film, at least

a step of cleaning by an alkaline solution and
a step of cleaning by an acidic solution.

METHOD FOR CLEANING SUBSTRATEABSTRACT OF THE DISCLOSURE

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A method of cleaning the surface of a substrate, wherein the first step of the process of cleaning the substrate including a step of cleaning the surface of the substrate by an acidic solution, oxidizing solution, or
10 alkaline solution, comprises a step of removing the natural oxide film formed on the surface of the substrate.

FIG. 1

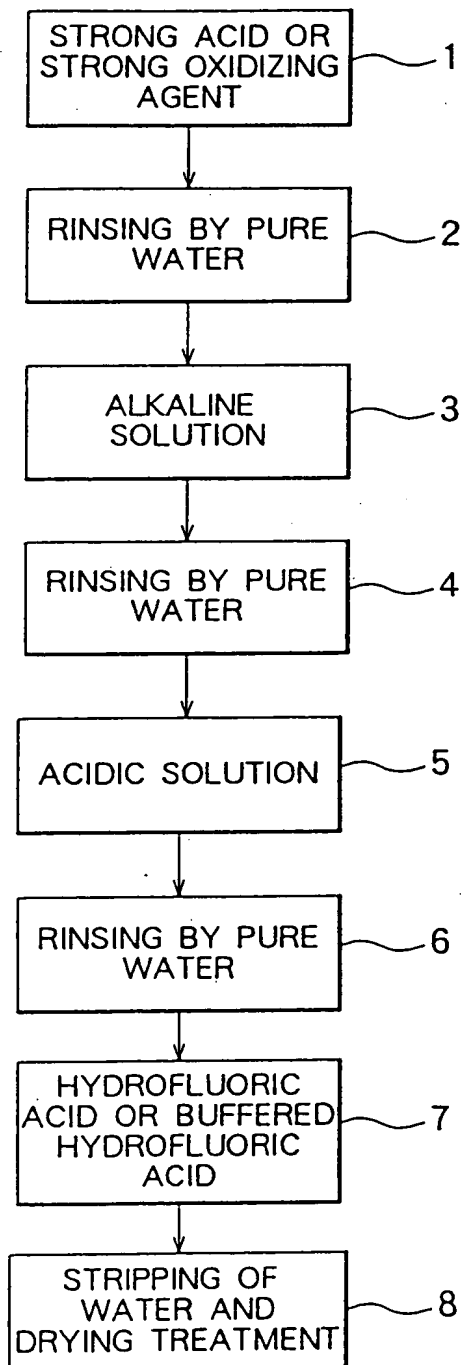


FIG. 2

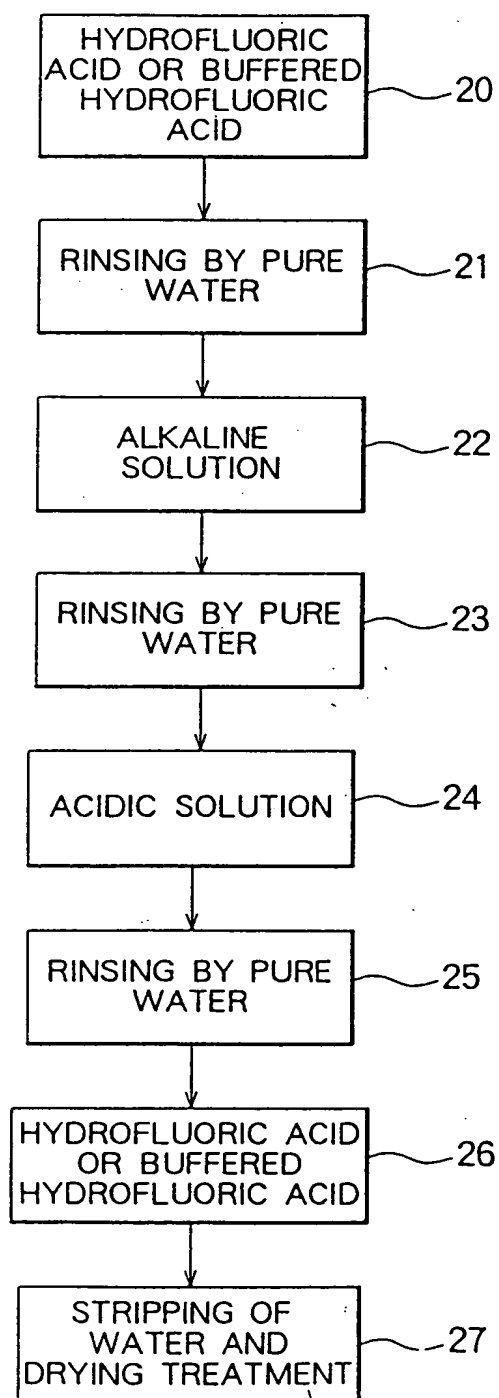


FIG. 3A

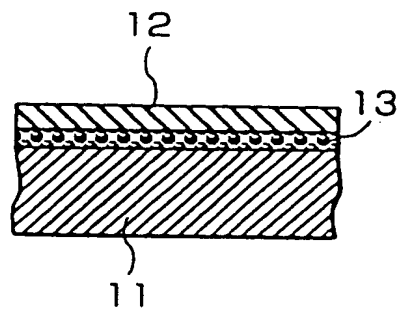


FIG. 3B

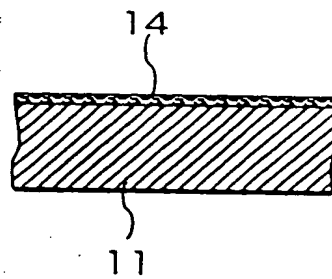


FIG. 3C

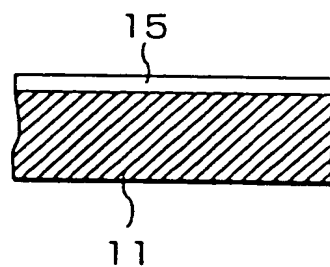


FIG. 3D

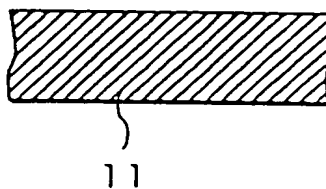


FIG. 4

